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Research Article

P123 assisted synthesis and characterization of urchin-like γ-Al_2O_3 hollow microspheres

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Abstract: Hierarchical urchin-like γ-Al_2O_3 hollow microspheres were prepared by a hydrothermal method followed by a calcination process using $Al(NO_3)_3·9H_2O$ as aluminum source, $NH_3·H_2O$ as precipitating agent, and P123 as structure-directing agent (SDA). The obtained samples were investigated using X-ray diffraction (XRD), filed emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and N_2 adsorption/desorption. The influences of P123 concentration, acidic condition, and hydrothermal time on the morphology of product were discussed. P123 has a great influence on ruling the oriented attachment of nanowires and stabilizing the superstructure in the self-assembly process. The 3D urchin-like hollow microspheres have a surface area of 210.2 m^2/g and the average pore size is 11.42 nm, which have widely potential application such as catalyst, adsorption, and separation.

Keywords: γ-Al_2O_3; hydrothermal method; hollow microspheres; urchin-like; crystal growth

1 Introduction

Recently, materials of inorganic hollow sphere structures [1–3] have received increasing attention. These structures have low density, high specific surface area, hollow structure, and nanostructured wall, which can offer novel properties and expand potential application. γ-Al_2O_3 as one of the most important metal oxides, is widely used as catalyst, catalyst support, separation, and adsorbent due to its unique physico-chemical properties and low cost [4–7]. The synthesis of hierarchical structured γ-Al_2O_3 hollow mircospheres with tailored texture and morphology has attracted a great deal of concerns in recent years. The excellent performance of alumina is affected by its porous superstructure and morphological characteristics. Therefore, it is crucial to control the shape and size of γ-Al_2O_3 hollow spherical materials before use.

Up to date, a variety of hollow microsphere oxides [8,9] have been successfully fabricated by a hydrothermal method with assistance of organic structure-directing agents. The most commonly used templates are surfactants, such as triblock copolymers P123 [10,11], cetyl trimethylammonium bromide (CTAB) [12], F127 [13,14], and polyethylene glycol (PEG) [15]. Some research indicated that P123 ($(PEO)_{20}$–$(PPO)_{70}$–$(PEO)_{20}$) has advantages of adjusting texture and porous structures [16,17] and being produced at large scale. It is capable of building diverse aggregations in polar medium [18,19], which contains a hydrophilic (poly (ethylene oxide), PEO) block and a hydrophobic (poly (propylene oxide), PPO) block. During the dispersing process, P123

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aggregations would affect the surface tension of metal droplets, resulting in special structured nanomaterial. For preparing alumina hollow microspheres, self-encapsulated hollow structures have been synthesized successfully by hydrothermal method in the presence of PS-b-PHEA amphiphilic block copolymer as the structure-directing reagent [20]. Hu *et al*. [5] reported the preparation of alumina hollow nanospheres via surfactant-assisted flame spray pyrolysis. However, there has been rare report on the fabrication of urchin-like γ-Al_2O_3 hollow microsphere nanostructures by using P123 as surfactant.

In this study, the self-assembly urchin-like γ-Al_2O_3 hollow microspheres were prepared by a simple hydrothermal method followed by a calcination process using $Al(NO_3)_3·9H_2O$ as aluminum source, $NH_3·H_2O$ as precipitating agent, and P123 as structure-directing agent (SDA). The effects of surfactant concentration, pH value, and hydrothermal time on the textural and structural evolutions of alumina hollow microspheres were investigated in detail. Moreover, the formation mechanism of urchin-like γ-Al_2O_3 hollow microspheres was also discussed.

2 Experiment

In a typical procedure, analytical pure $Al(NO_3)_3·9H_2O$ (3 mmol) was dissolved into 50 mL distilled water at room temperature in a beaker to form a homogeneous solution. $NH_3·H_2O$ (45 mmol) was subsequently dropped into the solution, giving rise to milky precipitates at pH = 4. Then, $(PEO)_{20}$–$(PPO)_{70}$–$(PEO)_{20}$ block copolymer (Pluronic P123) was dissolved in reaction mixture under vigorous magnetic stirring. After that, the resultant mixed solution was transferred into a 100 mL Teflon-lined stainless autoclave. Experiment conditions were controlled at 180 ℃ for 24 h with autogenous pressure in an electric oven, and then cooled to room temperature naturally. The obtained products were washed for several times by distilled water and ethanol and dried at 60 ℃ for 12 h. Finally, the calcined products were fabricated at 600 ℃ for 2 h.

Phase identification of the as-prepared samples were analyzed by X-ray diffraction (XRD, D/Max-RB, Japan) using Cu Kα radiation (λ = 0.154178 nm). The morphologies were observed by filed emission scanning electron microscopy (FESEM, FEI-Sirion200, Amsterdam, the Netherlands), and transmission electron microscopy (TEM, JEM-2010F, JEOL, Tokyo, Japan). Nitrogen adsorption/desorption measurements were evaluated at 77 K with a Micromeritics ASAP 2020 adsorption analyzer (USA). The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The Barrett–Joyner–Halenda (BJH) model was utilized to demonstrate the pore size distribution.

3 Results and discussion

Figure 1 shows the XRD patterns of the products fabricated before ((a) and (b)) and after ((c) and (d)) calcination at 600 ℃ for 2 h (hydrothermal reaction condition: pH = 4, 180 ℃, 24 h). All the diffraction peaks reflected in Figs. 1(a) and 1(b) are identified as orthorhombic γ-AlOOH (JCPDS Card No. 21-1307). Figures 1(c) and 1(d) can be indexed to the cubic γ-Al_2O_3 (JCPDS Card No.10-0425) with lattice constants of a = 7.9 Å, b = 7.9 Å, and c = 7.9 Å, indicating a complete conversion from γ-AlOOH to γ-Al_2O_3 via calcination. No obvious XRD peaks arising from impurities are observed.

Figure 2 shows the FESEM and TEM images of samples prepared at pH = 4 with 1 g P123 before and after calcination (hydrothermal reaction condition: 180 ℃, 24 h). Figure 2(a) shows that the sample consists of uniform urchin-like microsphere architectures with an average diameter of 2.5 μm. The high-magnification FESEM image of single architecture (Fig. 2(b)) reveals that the microsphere is

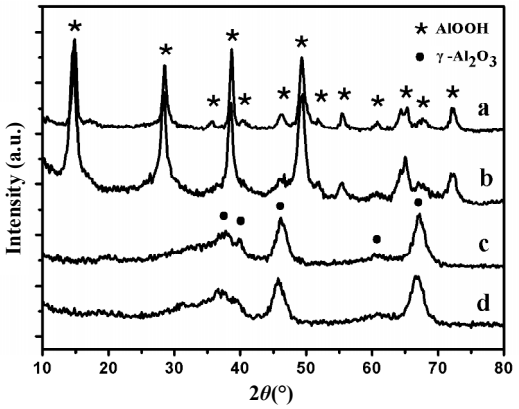

Fig. 1 XRD patterns of the products obtained at 180 ℃ for 24 h and pH = 4: before calcination (a) without P123 and (b) adding 1 g P123, after calcination (c) without P123 and (d) adding 1 g P123.

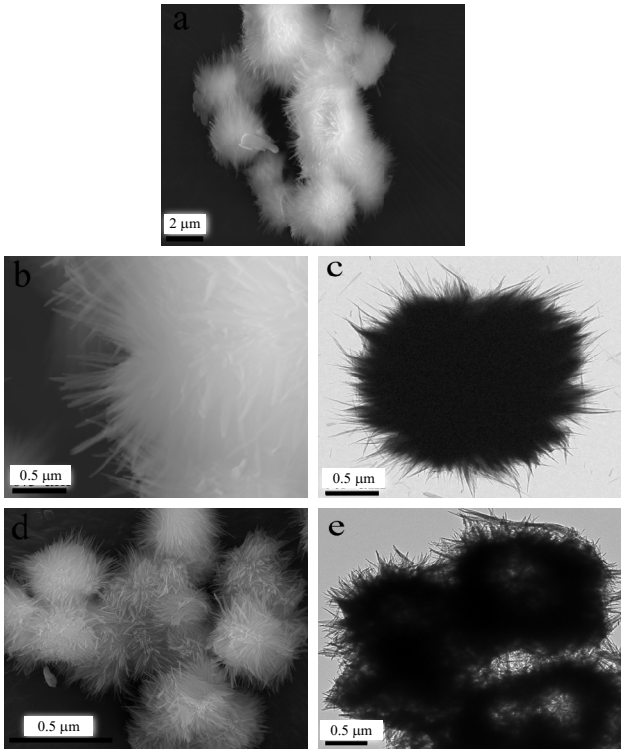

Fig. 2 (a, b, d) FESEM and (c, e) TEM images of the products with 1 g P123 (hydrothermal reaction condition: pH = 4, 180 ℃, 24 h): before (a, b, c) and after (d, e) calcination.

comprised of a large number of well-aligned nanowires. The corresponding TEM image in Fig. 2(c) demonstrates that urchin-like microsphere has a solid structure before calcination.

The typical FESEM and TEM images of the urchin-like γ-AlOOH microspheres after calcination at 600 ℃ are shown in Figs. 2(d) and 2(e) (hydrothermal reaction condition: pH = 4, 180 ℃, 24 h), respectively. Figure 2(d) shows that the microspheres have uniform shape and keep the urchin-like morphology after calcination. These microspheres turn to hollow structure, which is confirmed by the corresponding TEM image (Fig. 2(e)). The actual structures of the urchin-like hollow microspheres with obvious contrast between dark edge and pale center are also revealed in Fig. 2(e). The pale center of the urchin-like hollow microsphere is formed by interlacing and connecting pores of different sizes and shapes. The formation of hollow microsphere is due to vapor diffusion during calcination [5,21,22]. The vapor diffusion is conducive to the formation of a uniform porous structure at dehydration process. After the phase transformation of γ-AlOOH to γ-Al_2O_3 at 600 ℃, the porous frameworks become stable and 3D superstructure is formed.

In order to investigate the influence of pH value on the formation of the γ-Al_2O_3 hollow microspheres, different experiments were carried out by changing the pH value. Figure 3(a) displays the TEM image of the γ-AlOOH prepared at pH = 6 with 1 g P123 (hydrothermal reaction time: 180 ℃, 24 h). Some nanowires with a length-to-diameter ratio of approximately 30 are formed and aggregated with each other. Microscopy analysis also reveals that no urchin-like hollow microsphere is formed. When the pH value increases to 8, TEM image (Fig. 3(b)) demonstrates that nanoflakes with a length of 40–50 nm are formed. Morphologies of samples shown in Figs. 3(c) and 3(d) reveal the size and shape of these products obtained at pH = 6 and 8 after calcination, respectively. When the pH is changed to lower values (pH = 2), no precipitates are observed in the solution after hydrothermal reaction. γ-AlOOH nanowires with a large length-to-diameter ratio, which are only obtained in a narrow pH value range, could be attributed to the 3D framework structure of boehmite. Meanwhile, acidic condition may have effect on the oriented attachment of P123 and benefit to 3D urchin-like hollow superstructure.

In order to investigate the effects of P123 concentration on the product morphologies, a series of calcined γ-Al_2O_3 samples were prepared under basic condition (hydrothermal reaction condition: pH = 4, 180 ℃, 24 h). Their TEM images are displayed in Fig. 4.

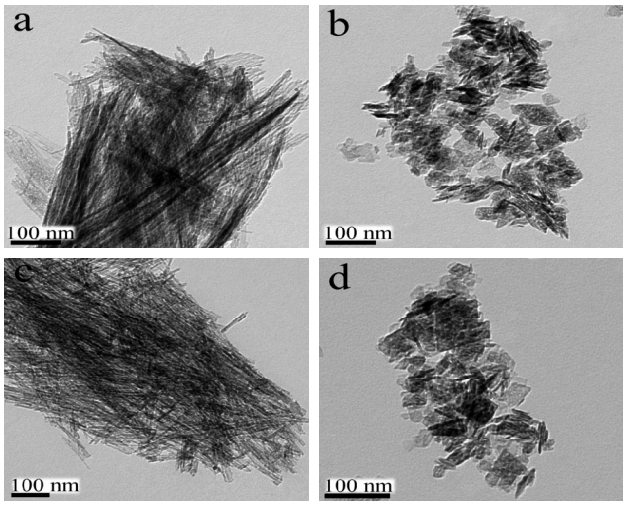

Fig. 3 TEM images of the products with 1 g P123 under different acidic conditions: before calcination (a) pH = 6 and (b) pH = 8, after calcination (c) pH = 6 and (d) pH = 8 (hydrothermal reaction condition: 180 ℃, 24 h).

When P123 is not used, the aggregated γ-Al_2O_3 nanowires are formed, which probably result from the hydrogen bonds. TEM image in Fig. 4(a) clearly demonstrates that no self-assembly process occurs. When 1 g P123 is added, the TEM image of the sample (Fig. 4(b)) illustrates that the calcined γ-Al_2O_3 has urchin-like hollow structure. With the increase of P123 to 2 and 4 g, urchin-like hollow microspheres disappear and aggregated nanowires form (shown in Figs. 4(c) and 4(d), respectively), which is probably due to high P123 concentration.

Seen from the above experimental results, it is found that P123 may have dual functions in controlling the superstructure morphology at pH = 4: adjusting the oriented attachment of the nanowires and stabilizing the 3D superstructure [23,24]. When 1 g P123 is used (Fig. 4(b)), the role of P123 as structure-directing agent may be operiative. P123 may stabilize the superstructure by lowering its surface free energy because of coverage of P123 on the crystal surface [25]. When the usage of P123 is more than 2 g, it results in high solution viscosity because of the micellization behavior of the triblock copolymer [26]. The solution viscosity reduces the mobility of nanowires and hinders the self-assembly process. No self-assembly process occurs and the aggregation of nanowires is observed in Figs. 4(c) and 4(d).

In order to reveal microsphere formation process, the time dependent experiments were done. The holding time is chosen as 2, 6, 8, 12, 24, and 48 h. Morphological evolution is analyzed by the TEM images in Figs. 5 and 6. As observed from Figs. 5(a) and 5(b), the uncalcined products obtained after hydrothermal treatment for 2 and 6 h respectively reveal scarve-like morphology. With the prolongation of time (8 h), the transformation of scarve-like structure to nanowires occurs by self-curl process (Fig. 5(c)). When hydrothermal treatment time reaches to 12 h (Fig. 5(d)), the urchin-like microsphere begins to appear. After calcination, urchin-like solid microsphere is transformed to urchin-like hollow microsphere (Fig. 6(d)). With the hydrothermal treatment continuing, the morphology of γ-Al_2O_3 hollow microsphere with porous structure keeps after calcination (Fig. 6(e)). When hydrothermal time is 48 h, nanowires with length of 700–800 nm are obtained (Fig. 5(f)), illustrating that the urchin-like hollow structure is metastable. Morphologies of calcined samples shown in Fig. 6 reveal the size and shape of these products obtained at 2, 6, 8, and 48 h kept after calcination. In the morphological evolution process, nanowires are the thermodynamically stable structure and urchin-like hollow structure is only a kinetic product.

As for the formation of the urchin-like γ-Al_2O_3 hollow microsphere, the complex structure may be constructed through the formation and self-assembly of nanowires. At the beginning, γ-AlOOH has a lamellar

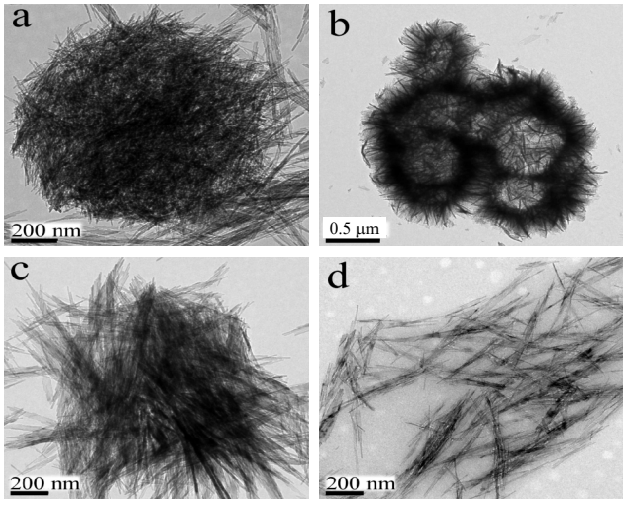

Fig. 4 TEM images of the calcined products with different amount of P123: (a) 0 g, (b) 1 g, (c) 2 g, (d) 4 g (hydrothermal reaction condition: pH = 4, 180 ℃, 24 h).

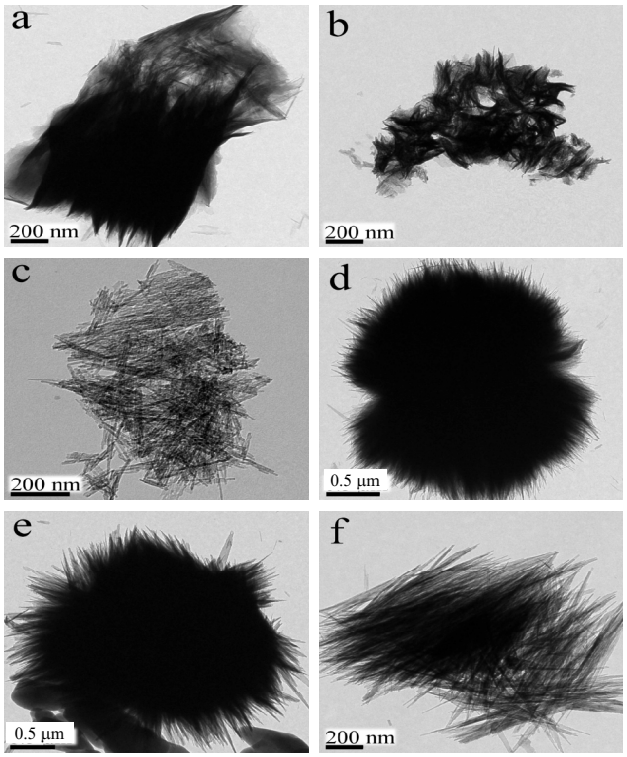

Fig. 5 TEM images of uncalcined products with 1 g P123 for different time: (a) 2 h, (b) 6 h, (c) 8 h, (d) 12 h, (e) 24 h, (f) 48 h (hydrothermal reaction condition: pH = 4, 180 ℃).

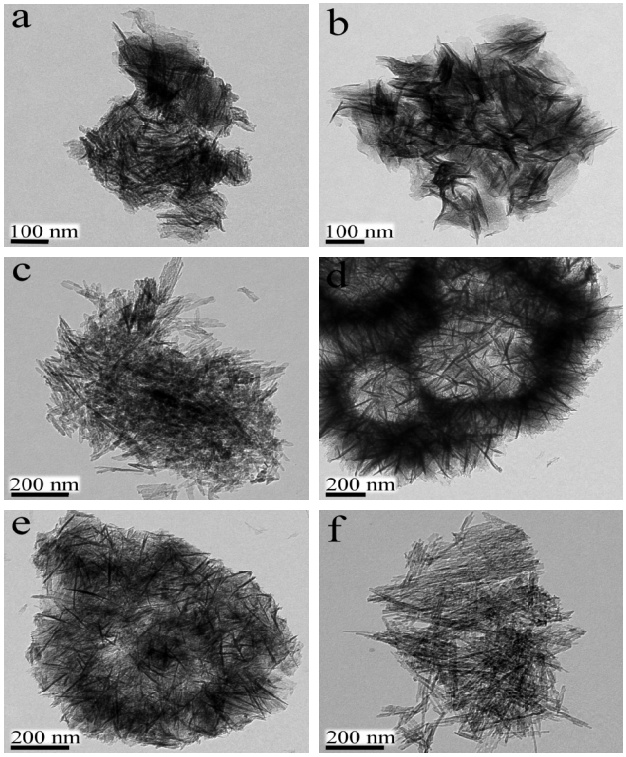

Fig. 6 TEM images of calcined products with 1 g P123 for different time: (a) 2 h, (b) 6 h, (c) 8 h, (d) 12 h, (e) 24 h, (f) 48 h (hydrothermal reaction condition: pH = 4, 180 ℃).

structure of linked octahedral AlO_6 units, which is easy to form an infinite plane perpendicular to [010] direction [27]. Hydroxyl groups sustain the lamellar structure by hydrogen bonding. Under acidic condition, the reaction mixture contains excess protons that would protonate the hydroxyl oxygen-lone pairs to produce aqua ligands, inducing the exfoliation of boehmite layers [28]. Hydroxyl groups of boehmite layer expose and subsequently bond together by hydrogen bonding to curl to form 1D structure. Meanwhile, H^+ existing under present acid condition may react with hydroxyl ions to limit or break the original hydrogen bonding between them due to the equilibrium of dissolution–precipitation, which also contributes to the growth of nanowires [27]. With the reaction further going on, the nanowires begin to self-assemble into urchin-like microsphere through oriented attachment. The driving force comes from the reduction of the surface free energy of the microsphere due to the coverage of P123 on the surface of γ-AlOOH. Finally, urchin-like γ-AlOOH solid microspheres transform into γ-Al_2O_3 hollow microspheres as chemistry reaction and vapor diffusion occur after calcination. Herein, complex urchin-like γ-Al_2O_3 hollow microspheres should be the product of cooperative functions of P123 and pH value.

The nature of the 3D urchin-like hollow structure was confirmed by measurement of the pore size distribution and specific surface area. Figure 7 shows the nitrogen adsorption/desorption isotherms and pore size distribution of the product calcined at 600 ℃ for 2 h (hydrothermal reaction condition: pH = 4, 180 ℃, 24 h, 1 g P123). The isotherms of 3D urchin-like hollow γ-Al_2O_3 with 1 g P123 (present as AP1) present type-H3 hysteresis loop which is often associated with slit-like pores as a result of the aggregates of nanowires, illustrating the existence of micropores and mesopores [29]. Moreover, hysteresis loop of AP1 starts from low relative pressure, indicating that pore size of AP1 is small and the development of micropore in the AP1 [30]. Barrett–Joyner–Halenda (BJH) calculations for the corresponding pore size distribution (inset of Fig. 7) show distributions centered at 24.5 nm for AP1 and an average pore size is 11.42 nm. In addition, specific surface area and total pore volume for the 3D urchin-like hollow structure are 210.2 m^2/g and 1.19 cm^3/g respectively, illustrating that P123 is beneficial to form the interconnected porous network, which is in agreement with TEM results.

4 Conclusions

In summary, the self-assembly urchin-like γ-Al_2O_3 hollow microspheres were prepared by a simple hydrothermal method (hydrothermal reaction condition: pH = 4, 180 ℃, 24 h) and using P123 as structure-directing agent after calcination (calcination condition: 600 ℃, 2 h). FESEM and TEM studies indicated that P123 plays a key role in determinating the oriented attachment of nanowires and stabilizing the

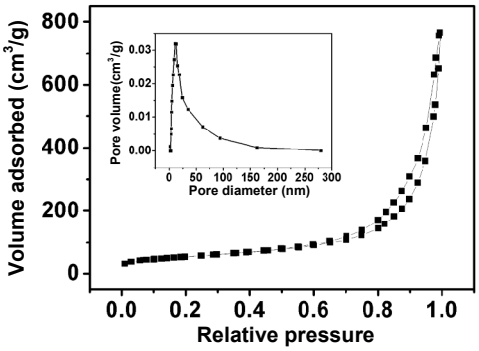

Fig. 7 Nitrogen adsorption/desorption isotherms of the calcined products with 1 g P123 (hydrothermal reaction condition: pH = 4, 180 ℃, 24 h).

superstructure in the self-assembly process. Moreover, the acidic condition and suitable SDA concentration were in favor of the formation of 3D urchin-like hollow microspheres which have high surface area and excellent porous structure.

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